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Fragmentation of Realgar, As_4S_4, Controlled by Transition Metal–Ligand Systems

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Abstract

The chemical behavior of the realgar molecule, As_4S_4, toward various (triphos)M moieties has been investigated. The reaction of As_4S_4 with [{MCl(cod)}$_2$] (M = Rh or Ir; cod = 1,5-cyclooctadiene) in the presence of the ligand triphos [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] yields compounds of formula $[(\text{triphos})M(\eta^3\text{-}As_3S_3)]\cdot C_6H_6$ containing the new As_3S_3 unit, which is trihapto bonded to the metal atom through one sulfur and two arsenic atoms. Such a As_3S_3 fragment is the largest one so far extruded from the realgar molecule. The As_4S_4 molecule undergoes more drastic disruptions in the reactions with $Co(BF_4)_2\cdot 6H_2O$ and $Ni(BF_4)_2\cdot 6H_2O$ in the presence of triphos. These results suggest that the fragmentation of the As_4S_4 molecule is controlled by the nature of the metal atom involved in the reaction.

Introduction

Cluster compounds in which main group elements and transition metal–ligand units form linkages to each other are receiving increasing interest. Such derivatives have remarkable and, in some cases, unusual geometries and may react with electrophilic or nucleophilic species giving rise to a rich and interesting chemistry [1].

Among such compounds those containing naked atoms of groups V or VI have been comparatively more investigated and are continuously growing in number [2]. Considerably less attention, on the other hand, has been devoted to compounds containing 'mixed' units, formed by unsubstituted chalcogen and pnicogen atoms bound *inter se* [3, 4]. However, compounds of the latter type are expected to attract more interest in the future as they often present unusual clusters formed by the above 'mixed' units and transition metal moieties and because they are endowed with selective reactivity on the chalcogen or pnicogen atoms [4d, 4e, 4g, 5]. Moreover, the inclusion in a chalcogen framework of phosphorus or arsenic atoms that have a high affinity toward group VI elements, should allow expansion of the well documented polychalcogenide chemistry [4a].

Both molecular, E_4X_3, and polymeric, E_2X_3, pnicogen chalcogenides (E = P, As; X = S, Se, Te) [3, 4] have been found to be useful starting materials for the generation of coordinated units formed by the above E and X atoms. The extrusion of ligands also from the realgar, As_4S_4, molecule has been recently reported [4c, 6]. The extruded fragments range from single sulfur atoms (μ-S) [6], through homoatomic units (μ-S_2, μ-As_2, η^3-As_3) [4c, 6] to mixed ligands of increasing nuclearity, from μ-AsS [4d] to μ-As_2S_3 [6]. On the other hand, no complex containing the intact As_4S_4 molecule as a ligand has been obtained.

Now we report that the reaction of realgar with metal–triphos systems [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] yields compounds which contain various arsenido-sulphido species.

Experimental

The ligand triphos [7] and the complexes [{MCl(cod)}$_2$] (M = Rh or Ir; cod = 1,5-cyclooctadiene) [8] were prepared according to published procedures. As_4S_4 was synthesized by reacting gray arsenic and sublimated sulfur in a 1:1 ratio under nitrogen in a sealed tube for five days at *ca.* 440 °C.

$^{31}P\{^1H\}$ NMR spectra were measured (at 32.19 MHz) on a Varian CFT 20 spectrometer. ^{31}P positive chemical shifts are downfield relative to H_3PO_4 at 0.0 ppm.

Reactions of As_4S_4 with (triphos)M Units (M = Co, Rh, Ir, Ni)

All reactions and manipulations were carried out under nitrogen. Finely powdered As_4S_4 (2 mmol) was suspended in benzene (20 cm^3) and added to: (a) a solution of [{MCl(cod)}$_2$] (M = Rh, Ir) (0.5 mmol) and triphos (1 mmol) in tetrahydrofuran (40 cm^3) and benzene (10 cm^3); (b) a solution of $M(BF_4)_2\cdot 6H_2O$ (M = Co, Ni) (1 mmol) in ethanol

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(5 cm^3) and triphos (1 mmol) in tetrahydrofuran (30 cm^3).

The resulting suspensions were refluxed overnight and filtered. The solid compounds [(triphos)M(η^3-As_3S_3)]·C_6H_6 [M = Rh (1), Ir (2)], [(triphos)Co(η^3-As_2S)]BF_4·C_2H_5OH (3) and [(triphos)Ni(μ, η^3-As_3)-Ni(triphos)]$(BF_4)_2$ (4) were obtained by concentrating the resulting solutions. The compounds were filtered, washed with ethanol, light petroleum (boiling point 40–70 °C) and dried.

Anal. Found: C, 50.0; H, 4.1; As, 19.7; P, 8.0; S, 8.3. Calc. for [(triphos)Rh(η^3-As_3S_3)]·C_6H_6 (1) $C_{47}H_{45}As_3P_3RhS_3$: C, 50.1; H, 4.0; As, 19.9; P, 8.2; S, 8.5%. Found: C, 46.2; H, 3.9; As, 18.2; P, 7.3; S, 7.6. Calc. for [(triphos)Ir(η^3-As_3S_3)]·C_6H_6 (2) $C_{47}H_{45}As_3IrP_3S_3$: C, 46.4; H, 3.7; As, 18.5; P, 7.6; S, 7.9%.

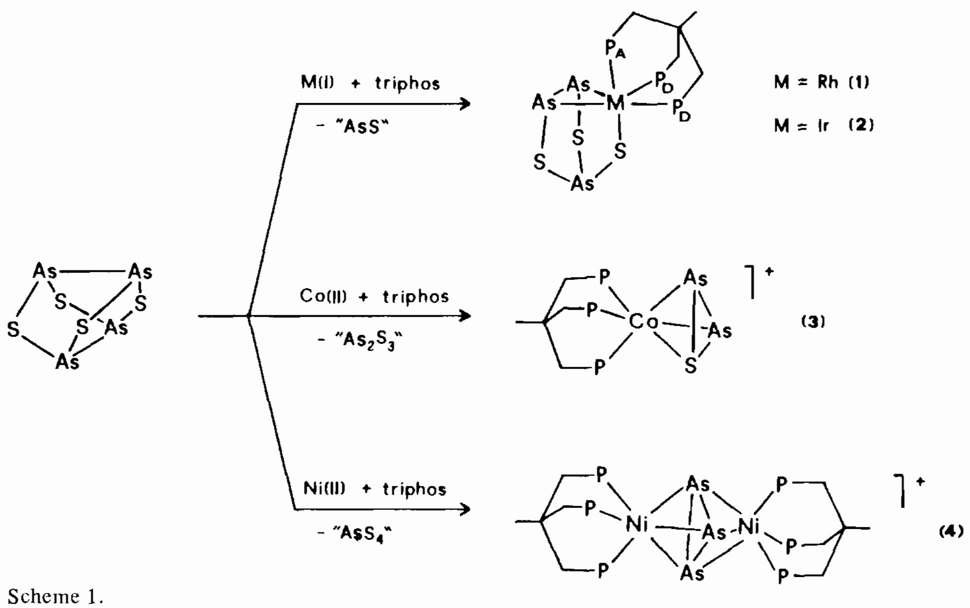
C, H, Co (or Ni), As, S elemental analyses for the compounds 3 and 4 agree with the values reported for the pure samples already described [4b, 9].

Results and Discussion

The reaction of [{MCl(cod)}$_2$] (M = Rh, Ir) in the presence of triphos with tetra-arsenic tetrasulfide, As_4S_4, affords the complexes of formula [(triphos)-M(η^3-As_3S_3)] [M = Rh (1), Ir (2)], which crystallize with one molecule of benzene. The diamagnetic compounds are stable in the solid state; they are slightly soluble in dichloromethane and 1,2-dichloroethane in which they behave as nonelectrolytes.

The rhodium compound, which is obtained in crystalline form, is isomorphous to the [(triphos)-Rh(η^3-P_3X_3)]·C_6H_6 (X = S, Se) derivatives and gives a diffraction pattern similar to those of the latter compounds. It is therefore safely assigned the same structure [3g], consisting of a (triphos)Rh moiety bound to one sulfur and two arsenic atoms of an As_3S_3 unit. The Ir derivative is also assigned this structure, based mainly on the elemental analysis and NMR data. Although the As_3S_3 unit originates from the As_4S_4 molecule by loss of one arsenic and one sulfur atom (Scheme 1) its geometry may be more closely related to that of the As_4S_3 cage molecule, assuming that one of the basal As atoms in the latter has been replaced by the (triphos)M system. Actually compounds 1 and 2 are also obtained by reacting the cage molecule As_4S_3 in the same conditions as As_4S_4 with [{MCl(cod)}$_2$] (M = Rh, Ir) in the presence of triphos. These alternative syntheses support the structural assignment made above. Considering that in the intact As_4S_4 molecule each As vertex is linked to one As and two S sites (Scheme 1), whereas in the As_3S_3 coordinating fragment one of the As atoms is bound to each one of the S sites, it is clear that the formation of the As_3S_3 unit in compounds 1 and 2 from the As_4S_4 molecule requires significant rearrangements of bonds between the arsenic and sulfur atoms, besides the elimination of an 'AsS' group.

The $^{31}P\{^1H\}$ NMR spectra in dichloromethane at room temperature exhibit an AD_2X pattern for 1 [δ P_A = 16.8t; δ P_D = −8.1d; $^2J(P_A, P_D)$ = 33 Hz; $^1J(P_A, Rh)$ = 103 Hz; $^1J(P_D, Rh)$ = 108 Hz] and an AD_2 system for 2 [δ P_A = −19.8t; δ P_D = −35.9d; $^2J(P_A, P_D)$ = 21 Hz]. All P(triphos) chemical shifts decrease consistently going from the rhodium to the iridium compound. The chemical shifts of the phosphorus atoms lying *trans* to arsenic occur at significantly higher fields than the shifts of the phosphorus atoms *trans* to sulfur. The coupling constants, of both



Scheme 1.

the ^1J(P, Rh) and ^2J(P, P) types, have values in agreement with those reported in the literature [10].

Compounds **3** and **4**, respectively containing the heterocyclic thiadiarsirene unit η^3 bound to the cobalt(triphos) moiety and the homocyclic triarsirene unit bridging two nickel(triphos) moieties (Scheme 1), have been characterized by comparing their elemental analyses and physical properties (conductivity measurements, IR, electronic, and nuclear magnetic resonance spectra) with those of the authentic samples [4b, 9]. All reactions described here, occurring between realgar and (triphos)M moieties (M = Rh, Ir, Co, Ni) are summarized in Scheme 1.

In conclusion, the As_4S_4 molecule yields different fragments in the presence of various (triphos)M moieties, depending on the nature of the metal atom and its oxidation state in the parent compound. The reactions with rhodium(I) and iridium(I) compounds give products containing the As_3S_3 fragment (yields *ca.* 30% for **1** and **2**) which preserves in part the structure of the original cage molecule and is the largest fragment so far stabilized after cleavage of As_4S_4 by metal ligand systems [6]. The cobalt(II) system, on the other hand, produces a drastic cleavage of the realgar molecule yielding in very good yield (*ca.* 70%) compound **3**, which contains the As_2S cyclic unit. Finally nickel(II) produces an even more profound disruption of the As_4S_4 molecule extruding from it the components of the homoatomic As_3 fragment (yield *ca.* 50%).

The present results illustrate two quite different stages of the process of attack of the pnicogen chalcogenide cage molecules by metal–triphos systems. In the formation of the As_3S_3 derivatives from the As_4S_4 substrate a considerable part of the original molecule is preserved although some rearrangement is also involved, which is larger, in particular, than that occurring when the same As_3S_3 fragment is formed from the As_4S_3 cage. A quite different picture is provided by the processes, presumably directed by metal–ligand systems with the metal atoms in comparatively high oxidation states, in which the As_2S and As_3 smaller fragments are formed. The high yields obtained also in the latter reactions show that cleavage of the cage molecule to fragments bearing little or no resemblance to the original structure is a rather easy process in the presence of coordinatively unsaturated metal centres.

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